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ABSTRACT

Nitrogen bearing species are common tracers of the physical conditions in a wide variety of objects, and most remarkably in dark clouds. The reservoir of gaseous nitrogen is expected to be atomic or molecular, but none of the two species are observable in the dark gas. Their abundances therefore derive indirectly from those of N-bearing species through chemical modelling. The recent years have accumulated data which stress our incomplete understanding of the nitrogen chemistry in dark cloud conditions. To tackle this problem of the nitrogen chemistry in cold gas, we have revised the formation of nitrogen hydrides, which is initiated by the key reaction $N^+ + H_2 \longrightarrow NH^+ + H$. We propose a new rate for this reaction which depends on the ortho-to-para ratio of H_2. This new rate allows to reproduce the abundance ratios of the three nitrogen hydrides, NH, NH_2, and NH_3, observed towards IRAS16293-2422, provided that the channel leading to NH from the dissociative recombination of N_2H^+ is not closed at low temperature. The ortho-to-para ratio of H_2 is constrained to $O/P = 10^{-3}$ by the abundance ratio NH:NH_2, which provides a new method to measure O/P. This work stresses the need for reaction rates at the low temperatures of dark clouds, and for branching ratios of critical dissociative recombination reactions.

Key words. ISM: Astrochemistry, abundances, ISM individual objects: IRAS 16293-2422

1. Introduction

Chemistry in an astrophysical context is not only a matter in itself but also provides invaluable tools to determine physical conditions such as volume density and kinetic temperature (Bergin & Tafalla 2007). Astrochemistry relies on chemical networks which depend on the type of environment (*e.g.* diffuse *vs* dense gas). The kinetic rates of the reactions are, in the best cases, based on thermodynamical and quantum mechanical calculations and experiments, which make the setup of such chemical networks an extremely demanding process. Various such networks of reactions are publicly available (KIDA, UMIST, OSU[1], Flower & Pineau des Forêts[2]), with various degrees of complexity and/or completeness regarding specific aspects of the chemistry (*e.g.* deuteration, cations...).

The nitrogen element is among the 5th or 6th most abundant in the Solar neighbourhood, after H, He, C, O, and probably Ne (Asplund et al. 2009; Nieva & Simón-Díaz 2011). In the cold neutral medium, nitrogen is expected to be predominantly atomic or molecular, but direct observations of N or N_2 are not possible. The amount of gaseous nitrogen thus relies on the abundances of N-bearing molecules *via* chemical models. Nitrogen bearing molecules are observed in a wide variety of physical conditions. Molecules such as CN, HCN, and HNC, with large permanent dipole moments, are detected towards diffuse clouds (Liszt & Lucas 2001), dense cores (Tafalla et al. 2004), protoplanetary disks (Kastner et al. 2008) and high-z galaxies (Guélin et al. 2007). N-bearing species, such as N_2H^+ (and its deuterated isotopologues), are also efficient tracers of the dense and cold gas where CO has already frozen-out (Crapsi et al. 2007; Hily-Blant et al. 2008, 2010b). The cyanide radical CN is also a precious molecule which serves as a tracer of the magnetic fields through Zeeman splitting (Crutcher et al. 2010). Understanding the chemistry of nitrogen is thus crucial in many astrophysical areas.

Ammonia and N_2H^+ are daughter molecules of N_2, which forms from atomic N through neutral-neutral reactions mediated by CN and NO (Pineau des Forêts et al. 1990). The formation of CN and the related HCN and HNC molecules, and in particular their abundance ratio CN:HCN, are however not fully understood (Hily-Blant et al. 2010b). The formation of ammonia in dark and dense gas is thought to take place in the gas phase. Once N_2 exists in the gas phase, it reacts with He^+ ions formed by cosmic-ray ionization, to form N^+ which by subsequent hydrogen abstractions lead to NH_4^+ and finally NH_3 by dissociative recombination. Le Bourlot (1991) (LB91 in the remainder of the paper) was the first to investigate the influence of the H_2 ortho-to-para ratio (noted O/P) on the formation rate of NH_3. LB91 considered the conversion between p$-H_2$ and o$-H_2$ through proton exchange in the gas phase. He concluded that when $O/P \geq 10^{-3}$, the formation of ammonia no longer depends on the value of O/P. However, a better test of the nitrogen chemistry is provided by the simultaneous observations of all three nitrogen hydrides, NH, NH_2, and NH_3 (*e.g.*, Persson et al. 2010). The Herschel/HIFI instrument has opened the THz window which contains the fundamental rotational transitions of light molecules with large electric dipole moments such as hydrides. Hily-Blant et al. (2010a, Paper I in what follows) have detected NH, NH_2, and NH_3 in the cold envelope of the Class 0 protostar IRAS16293-2422. The hyperfine structures of the $N = 1 - 0$ transitions of NH and NH_2 are seen for the first time, in absorption, and allow a precise determination of their excitation temperature (T_{ex}) and line centre opacity. Four lines of ammonia are also detected in absorption, plus the fundamental rotational transition at 572 GHz which evidences a self-

[1] `http://kida.obs.u-bordeaux1.fr`, `http://www.udfa.net/`, `http://www.physics.ohio-state.edu/~eric`
[2] `http://massey.dur.ac.uk/drf/protostellar/`

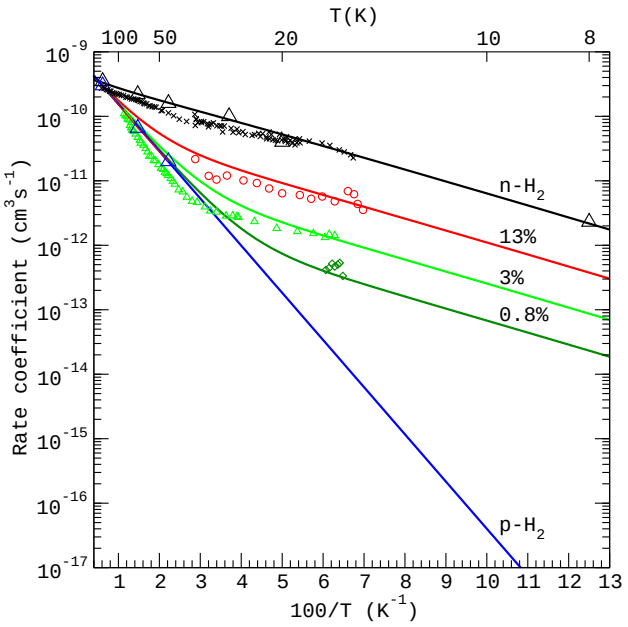

Fig. 1. Comparison of the rate coefficient as given by Eq. 3 to experimental data for the reaction of N^+ with n−H_2 and p−H_2 with different o−H_2 admixtures: 13%, 3%, 0.8%, and 0% (blue line). The small symbols are taken from Gerlich (1993) while the large triangles are CRESU results from Marquette et al. (1988). The solid lines correspond to Eq. 3 of the present paper.

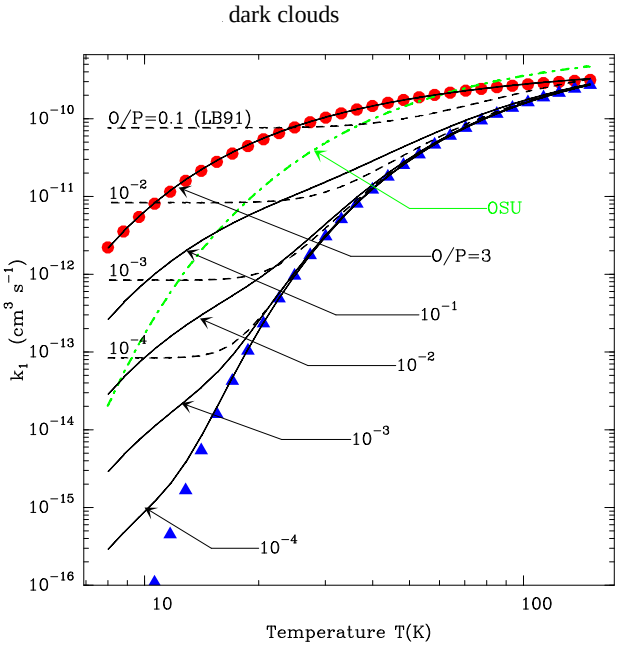

Fig. 2. Comparison of the rate coefficient for reaction (1) as given by Eq. 3 to the rates from LB91 (dashed) and the OSU database (dot-dashed). The rates are computed for temperatures in the range 8–150 K and O/P = 10^{-4}, 10^{-3}, 0.01, 0.1, and 3 (black lines). The symbols show the fits from Marquette et al. (1988) for normal H_2 (red circles, O/P=3) and p-H_2 (blue triangles).

absorbed line profile, likely tracing both warm and cold gas. For all three molecules, excitation temperatures were found in the range 8–10 K (Paper I). The derived column density ratios are NH : NH_2 : NH_3 = 5 : 1 : 300. Whilst abundances are generally delicate to derive because the column density of H_2 is uncertain, the column density ratios above provide a stringent test for the first steps of the nitrogen chemistry and for the ammonia synthesis in particular. Indeed, the current nitrogen networks available all produce more NH_2 than NH under dark cloud conditions (Paper I), at odds with the observations.

In this Letter, we investigate the NH:NH_2 problem in dark gas, by revisiting the kinetic rate for the reaction

$$N^+ + H_2 \longrightarrow NH^+ + H \qquad (1)$$

We derive separate rates for reaction with p- and o−H_2 for which the nuclear spin $I = 0$ and 1 respectively. In Section 2 we describe the new rates which are compared to experimental measurements and derive the abundances of nitrogen hydrides in typical dark cloud conditions. The results are discussed in Section 3 and we propose conclusion remarks in Section 4.

2. Chemical modelling

2.1. Rate of reaction $N^+ + H_2$

Reaction (1) has a small activation energy in the range 130-380 K (Gerlich 1993), with a consensus now tending towards a value below 200 K (*e.g.* Gerlich 2008). This reaction has been studied experimentally by Marquette et al. (1988) who considered pure para-H_2 and a 3:1 mixture of o- and p−H_2, refered to as normal H_2 (n−H_2). These authors fitted the two rates with normal and p−H_2 as $k_n = 4.16\times10^{-10}\,\exp[-41.9/T]$ cm^3 s^{-1} and $k_p = 8.35\times10^{-10}\,\exp[-168.5/T]$ cm^3 s^{-1}. The rate with p-H_2 was used by LB91, who assumed that the reaction with o−H_2 proceeds with no endothermicity, on the basis that the 170.51 K internal energy of the $J = 1$ level of o−H_2 is used to overcome the endothermicity. Accordingly, the rate of reaction (1) was written as $k_{\rm LB91} = 8.35\times10^{-10}[x + (1-x)\exp(-168.5/T)]$, where $x = {\rm O/P}/(1+{\rm O/P})$ is the fraction of o−H_2. Actually, the expressions for k_n and k_p allow to derive a simple expression for k_o, the reaction rate of N^+ with o−H_2, namely $k_n = 3/4\,k_o + 1/4\,k_p$ (Gerlich 1989). For O/P=3:1 and at temperatures less than ≈ 40 K, the rate is essentially k_o, and k_n is thus a good approximation of k_o at the low temperatures ($T < 15$ K) of dark clouds. Alternatively, a single-exponential fit to k_o leads to (see Fig. A.1)

$$k_o = 4.2\times10^{-10}\,(T/300)^{-0.17}\,\exp[-44.5/T] \quad {\rm cm^3\,s^{-1}} \qquad (2)$$

The rate for reaction (1) with an H_2 admixture of arbitrary O/P is then obtained as

$$k_1 = x\,k_o + (1-x)\,k_p \qquad (3)$$

In Figure 1, the rate k_1 from Eq. 3 is compared to the experimental data of Marquette et al. (1988) for the reaction with n- and p-H_2 down to 8 K and 45 K respectively. Gerlich (1993) performed experiments with n−H_2 and with p−H_2 containing admixtures of o−H_2 (13%, 8%, and 0.8%), at temperatures down to 14 K. The agreement between our Eq. 3 and the three sets of p−H_2 data of Gerlich (1993) is excellent at temperatures below 20 K, and to within a factor of 2 up to 100 K. This suggests that Eq. 3 should be accurate to within a factor of 2-3 down to 10 K. On the other hand, this rate should not be employed above ∼ 150 K.

We compare, in Fig. 2, the rate given by Eq. 3 to $k_{\rm LB91}$ and to the rate given by the OSU database $k_{\rm OSU} = 8.35\times10^{-10}\,\exp[-85/T]\,{\rm cm^3\ s^{-1}}$. The rate is computed for several values of O/P. As expected, it converges towards the n-H_2 and p-H_2 rates for large (O/P=3) and small (O/P= 10^{-4}) values respectively. It is evident that LB91 overestimated the rate of reaction (1) by several orders of magnitude at temperatures smaller than 20 K. In warmer gas ($T > 20$ K), k_1 and $k_{\rm LB91}$ agree

Table 1. Initial gas phase fractional abundances ($n(X)/n_H$) from Flower & Pineau des Forêts (2003) with $n_H = n(H) + 2n(H_2)$. For comparison, the fractional abundances from the low-metal model of Wakelam & Herbst (2008) are also given. Numbers in parentheses are powers of 10.

Species	Flower 2003	Wakelam 2008
H_2	0.50	0.50
He	0.10	0.14
N	6.39(-5)	2.14(-5)
O	1.24(-4)	1.76(-4)
C^+	8.27(-5)	7.30(-5)
S^+	1.47(-5)	8.00(-8)
Si^+	8.00(-9)	8.00(-9)
Fe^+	3.00(-9)	3.00(-9)
Mg^+	7.00(-9)	7.00(-9)

to within a factor of 10 or less, whilst the OSU rate approaches the O/P=3 curve. The OSU rate thus amounts to assume O/P ratios larger than 0.01, whereas LB91 provides acceptable rates only at temperatures larger than 20 K.

2.2. Abundance of nitrogen hydrides

In this work, we wish to reproduce the ratios NH:NH_2:NH_3 observed in the cold envelope of IRAS16293-2422 (Paper I). The fundamental hyperfine transitions of NH, NH_2 and several transitions of NH_3 have been detected in absorption. Absorption is interpreted as resulting from the low temperature of the gas in the envelope seen against the warmer continuum emitted by the dust closer to the protostar. The gas density is low (10^4-10^5 cm^{-3}) as compared to the critical density of the detected transitions ($> 10^7$ cm^{-3}) which ensures that collisions do not govern the (de)excitation processes. The $N = 1 - 0$ transitions are therefore thermalized with the dust emission temperature which, in the THz domain, correspond to excitation temperatures close to a kinetic temperature of 10 K. The lines are Gaussian and do not show signatures of strong dynamical effects such as infall. Dynamical timescales are then expected to be large with respect to the free-fall time. The observed lines therefore trace a cold gas, moderately dense, free of dissociating photons, and where the ionization is driven by cosmic rays.

The main point raised by Paper I is that the observed ratios NH:NH_2:NH_3=5:1:300 could not be reproduced by chemical networks updated regarding the rates of the dissociative recombination (DR) reactions leading to NH, NH_2, and ammonia. Paper I considered three models, with varying branching ratios for some DR reactions. Whilst the NH_2:NH_3 abundance ratio could be reproduced in all three cases, no model was able to produce[3] [NH] > [NH_2]. These models used the OSU rate for reaction (1) which was shown in Sec. 2.1 to depart from the measured rate by several orders of magnitude in cold gas and O/P smaller than 0.01. The next Section explores the consequence of the new rate given by Eq. 3 on the abundances of the nitrogen hydrides, in typical dark cloud conditions.

We have performed chemical calculations in a gas at $T = 10$ K, with density $n_H = 10^4$ cm^{-3}. The gas is screened by 10 mag of visual extinction, such that the ionization is primarily due to cosmic rays at an adopted rate $\zeta = 1.3\times10^{-17}$ s^{-1}. Gas-phase abundances are computed as a function of time by solving the chemical network until steady-state is reached. Freeze-out of gas-phase species onto dust grains are ignored in this work. In what follows, the quoted abundances correspond to the steady-state. The initial fractional elemental abundances (n_X/n_H) are the gas phase abundances taken from Flower & Pineau des Forêts (2003, hereafter FPdF03) who considered the depletion of metals in grain mantles, grain cores, and PAHs (see Table 1). These abundances differ from those adopted in Paper I (Wakelam & Herbst 2008). The rates for the dissociative recombination reactions are those of the model 1 of Paper I. From the above, the rate for the key reaction (1) depends on the O/P which is not known, but which might strongly differ from the thermodynamical equilibrium value (Maret & Bergin 2007; Pagani et al. 2009; Troscompt et al. 2009) which is $\approx 10^{-7}$ at 10 K. The steady-state abundances of NH, NH_2, and NH_3 have thus been computed for various values of O/P in the range 10^{-7} to 3.

In this work, the DR of NH_4^+ has three output channels, NH_3 + H, NH_2 + H_2, and NH_2 + H + H (Öjekull et al. 2004). However, another channel may be NH + H + H_2 (Adams et al. 1991), but to our knowledge, no branching ratio is available in the litterature. Values up to 10% may be considered in a future work.

We first consider the case where the DR of N_2H^+ produces only N_2 + H (Adams et al. 2009). The resulting abundances are the dashed lines in Fig. 3. It appears that the O/P controls the abundances of NH, NH_2, and NH_3 but the ratios NH:NH_2 and NH_3:NH_2 are insensitive to O/P. In a second series of calculations, the NH + N channel is given a 10% branching ratio for the DR of N_2H^+. In this case, the abundance of NH is nearly independent of O/P, while the abundances of NH_2 and NH_3 remain unaffected (full lines in Fig. 3. As a consequence, it is found that for O/P < 0.03, NH : NH_2 > 1. In Paper I though, opening this channel did not solve the NH:NH_2 problem, which contrasts with the above result. This may be understood as follows. When the NH + H channel of the dissociative recombination of N_2H^+ is opened with a 10% braching ratio, the corresponding rate is $\approx 5.5\times10^{-8}$ cm^3 s^{-1}, several orders of magnitude larger than k_1 (see Fig. 2). Hence this channel, which is insensitive to O/P, dominates the formation of NH over $NH_2^+ + e^-$. In contrast, the other hydrides NH_2 and NH_3 are daughter molecules of NH^+ which is formed from $N^+ + H_2$ whose rate does explicitely depend on O/P in the present work. Hence the abundances of NH_2 and NH_3 do also depend on O/P. On the other hand, at the temperature of 10 K and O/P < 10^{-3}, the revised rate k_1 (Eq. 3) is at least an order of magnitude smaller than the OSU rate used in Paper I. For larger O/P, the rate is similar or even larger up to a factor of 10. These two effects, namely the drop of k_1 for low O/P, and the O/P-independant formation of NH, makes it possible to produce a NH:NH_2 ratio with values greater than unity. In the following we keep the NH + N channel opened to 10% and explore some consequences of this result.

3. Discussion

3.1. The H_2 O/P ratio in dark clouds

Computing the abundance ratios NH:NH_2 and NH_3:NH_2 for different O/P ratios leads to the left panel of Fig. 4. The initial fractional abundances are kept fixed, while the rate of reaction (1) is calculated for values of O/P from 10^{-7} (close to the Boltzmann value at 10 K) to 3. The calculated ratios are compared with the observational constraints. As expected, the NH_3:NH_2 ratio is insensitive to O/P variations. It is equal to 10, not consistent with the observed value of 300. On the contrary, the NH:NH_2

[3] Hereafter, the fractional abundance of species X is noted [X] and equals $n(X)/n_H$.

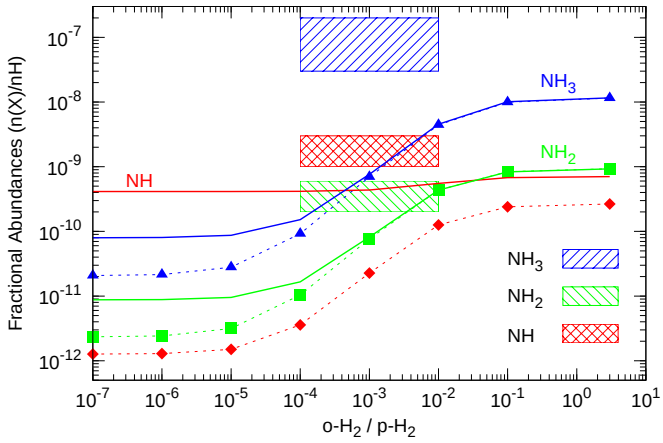

Fig. 3. Steady-state abundances (with respect to H nuclei) of nitrogen hydrides as a function of O/P, in a 10 K gas with $n_H = 10^4$ cm^{-3}, and $\zeta = 1.3\times10^{-17}$ s^{-1}. The rate of reaction (1) is given by Eq. 3. Two branching ratios for the channel $N_2H^+ + e^- \longrightarrow NH + N$ are considered: 0% (dashed lines) and 10% (full lines). The observed abundances from Paper I are also indicated (filled rectangles).

ratio shows two regimes: for O/P $< 10^{-5}$, NH : $NH_2 \approx 50$, and for O/P > 0.1, NH : $NH_2 \approx 0.07$. The observed ratio of 5 is intermediate, and indeed well constrains the O/P to 10^{-3}. From Fig. 4, we conclude that there is a range of O/P for which [NH] > [NH_2] and [NH] < [NH_3] simultaneously. In our case, this range is O/P = 5×10^{-4} – 0.02. The O/P ratio appears as a control parameter for the NH:NH_2 ratio, and allows for the first time to produce more NH than NH_2. Conversely, the measure of NH:NH_2 tightly constrains the O/P ratio. We note that the fractional abundance of NH_3 of 1.9×10^{-9}, measured by Crapsi et al. (2007) towards the starless core L 1544, corresponds to an O/P = 10^{-3} – 10^{-2}. This ratio is a factor of 10 larger than the corresponding ratio from the model of LB91. It is thus found that reaction (1) regulates the formation of NH_2 and NH_3 whilst the formation of NH is controlled by the dissociative recombination of N_2H^+ provided the branching ratio towards NH is 10%. The value of this branching ratio is uncertain but is likely non-zero (Adams et al. 2009).

3.2. Dependence on the initial abundances

The NH_3:NH_2 ratio is $\approx$ 10 in the above models, a factor 30 below the observed values towards IRAS16293-2422. However, models computed in Paper I with the initial abundances of Wakelam & Herbst (2008) lead to a ratio close to the observed value, hence suggesting that the initial elemental abundances influence this ratio. The gas phase elemental abundances of C, N, and O in dark clouds are poorly known because the amount of these elements incorporated into the dust (core or mantles) is loosely constrained. The elemental abundance of oxygen in the gas phase is not known accurately, and variations by an order of magnitude are fully conceivable (Jenkins 2009), whilst that of carbon is better known. Accordingly, we have considered variations of the initial elemental abundances of oxygen, to vary the ratio C:O, encompassing the value of 0.41 from Wakelam & Herbst (2008).

The resulting abundance ratios, computed for an O/P ratio of 10^{-3}, are shown in Fig. 4 (right panel). As C:O decreases below the 0.66 value of FPdF03, the ratio NH_2:NH_3 increases. In the process, NH:NH_2 remains constant. When C:O is now increased above 0.66, both ratios decrease, by at most a factor 2 to 5. It is thus apparent that, when [O] is increased, the C:O ratio controls the NH_2:NH_3 ratio. On chemical grounds, the C:O ratio is expected to influence the abundance of NH_2, for which the main destruction routes involve oxygen to form NO, NH, and HNO. Similarly, NH is mostly removed by reaction with oxygen to form principally NO. However, when oxygen is significantly depleted from the gas phase (C:O > 0.5), another destruction route of NH, involving sulfur, becomes important. As a result, the NH:NH_2 ratio is mostly insensitive to C:O, until C:O> 0.5 when it starts to decrease by small factors.

The situation is different for NH_3 which is destroyed by charge transfer reactions with H^+ and S^+ and by proton exchange reactions with H_3^+ and HCO^+, forming notably NH_4^+, which dissociates back into NH_3, and NH_3^+. A fraction of NH_3^+ will lead to NH_2 and NH which are the true destruction channels of ammonia. The abundance of NH_3 is thus only marginally affected by the change in C:O, unless the ionization fraction is modified, which is the case for low C:O ratios. An increase of the oxygen abundance (*i.e.* a decrease of C:O) is accompanied by a deacrease of [e^-], or equivalently [S^+] – the dominant ion – which makes the abundance of NH_3 to increase. Consequently, as C:O decreases below 0.66, NH:NH_2 keeps constant and NH_3:NH_2 increases by more than one order of magnitude. Whereas when C:O increases, NH:NH_2 decreases by less than a factor 10, whilst NH_3:NH_2 is approximately constant.

4. Conclusions

Using an updated rate for reaction (1) with an explicit dependence on the O/P ratio, we have shown that the O/P of H_2 controls the ratio NH:NH_2 in dark clouds without affecting the NH_3:NH_2 ratio. A value of O/P close to 10^{-3} leads to NH : NH_2 > 1 and NH_3 : NH_2 < 1 as observed. Interestingly, this value of O/P is close to the predictions of Flower et al. (2006, their Fig. 1) under similar conditions. In addition, measuring the NH:NH_2 ratio may be a new method to constrain the O/P ratio of H_2 in dark clouds. We have also shown that decreasing the C:O ratio by increasing [O] controls the NH_2:NH_3 ratio. Finally, acceptable parameters are found that lead to abundance ratios in agreement with the observations towards IRAS16293-2422, namely O/P $\approx$ 10^{-3} and C:O$\leq$ 0.4. It is to be noted, however, that in this range of parameters, the absolute abundances predicted by the models are a factor of 10 below those derived in Paper I.

In this work, the influence of O/P on the ratios NH:NH_2:NH_3 has been explored only through the rate of reaction (1). A better study would be to self-consistently compute the O/P ratio from a model of conversion of o–H_2 into p–H_2, as was first considered by LB91, and more recently by *e.g.* Pagani et al. (2009). Including proton exchange reactions, in the gas phase, between H_2 and H^+ (Honvault et al. 2011), H_2^+ (Crabtree et al. 2011), and H_3^+ (Hugo et al. 2009), would reprocess the 3:1 mixture of H_2 formed on grains to a different O/P. An even more self-consistent approach would be that of Flower et al. (2006) who separate reactions with the ortho- and para- forms of all concerned N-bearing molecules. Another obvious continuation would be to explore these findings in different physical conditions (A_V, cosmic-ray ionization rate, *etc*).

Branching ratios of dissociative recombination reactions are crucial to the formation of nitrogen hydrides. In this work, the dissociative recombination of NH_4^+ has three output channels

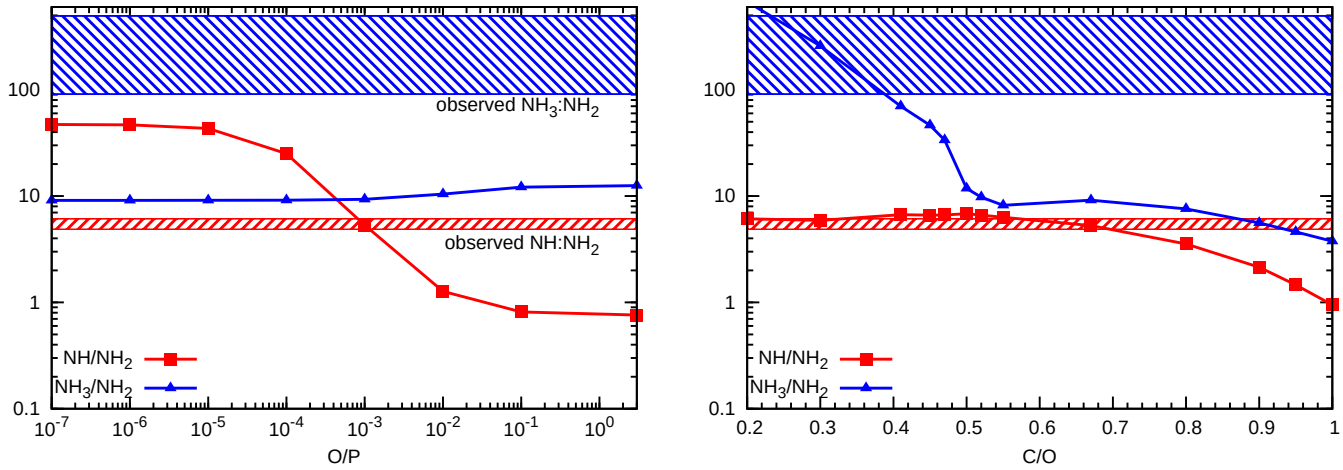

Fig. 4. Abundance ratios calculated when a 10% branching ratio is considered for the reaction $N_2H^+ + e^- \longrightarrow NH + H$. The hashed bands show the observed ratios with their 1σ uncertainties. *Left panel*: varying O/P, with the initial abundances of Flower & Pineau des Forêts (2003) ([O]=1.24(-4) and [C]=8.27(-5).). *Right panel*: varying [O] while keeping [C] constant, at constant O/P= 10^{-3}. The low-metal abundances of Wakelam & Herbst (2008) are [O]=1.76(-4) and [C]=7.30(-5), or C:O=0.41.

NH_3 + H, NH_2 + H_2, and NH_2 + H + H (Öjekull et al. 2004). However, another channel may be NH + H + H_2 (Adams et al. 1991), but to our knowledge, no branching ratio is available in the litterature. Values up to 10% may be considered in a future work. Critical too are the values of rates at low temperatures, especially for reaction (1) with p−H_2 for which measurements at temperatures lower than 14 K are not available.

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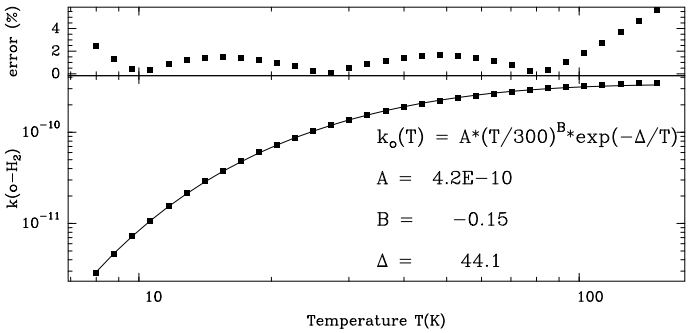

Fig. A.1. Rate for reaction (1) with o−H_2 and fit result (see Eq. 2). Bottom panel: filled squares are the values derived from Marquette et al. (1988), and the fitted curve (full line). Top panel: relative error.

Appendix A: Reaction rate

For the purpose of implementing the rate of the reaction (1) with ortho-H_2 in chemical networks, Figure A.1 shows the result of a single-exponential fit. The filled squares are based on the fitted reaction rates from Marquette et al. (1988). A weighting in the form $1/(T-10)^2$ was adopted, which is accurate to better than 6% for $T = 8 - 150$ K.